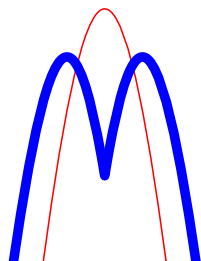


# MOLPRO



## *Recent Changes* *Version 2015.1*

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## New features of MOLPRO2015.1

Molpro 2015 contains many improvements, bug-fixes and new features. Only the most important ones are listed in the following.

### Projector-based wavefunction-in-DFT embedding

The WF-in-DFT implementation in Molpro [F. R. Manby et al., J. Chem. Theory Comput. **8**, 2564 (2012)] permits embedding of almost any ground-state wavefunction method in Molpro in an environment described by DFT.

### Intrinsic bond-orbital analysis and orbital localization (IBO).

IBOs provide a reliable and efficient way to generate localized orbitals and to analyze wavefunctions, see G. Knizia, J. Chem. Theory Comput. **9**, 4834 (2013)

### Interface to NBO6

Molpro 2015 supports NBO6 Natural Bond Orbital Analysis (NBO6) via an interface. NBO6 must be licensed separately.

### Beyond LMP2 treatment of intermolecular pairs in local coupled cluster methods

Usually close (and weak) pairs are treated only at the LMP2 level in LCCSD(T) calculations. This not satisfying since LMP2 often treats van der Waals interactions poorly, hence compromising the high accuracy of the actual LCCSD(T) calculation. Fortunately, close pairs can now be treated in an inexpensive way at a level beyond LMP2, ranging from local direct RPA *via* ring CCD to LCCD[S]-R<sup>-6</sup>. This is described in

O. Masur, D. Usvyat and M. Schütz, J. Chem. Phys., **139**, 164116 (2013);

M. Schütz, O. Masur and D. Usvyat, J. Chem. Phys., **140**, 244107 (2014).

### Distinguishable cluster Approximation (DCSD and DCSD-F12)

This approximation yields improved results at the cost of CCSD. In particular, DCSD equilibrium structures are as accurate as for CCSD(T), see

D. Kats and F. R. Manby, J. Chem. Phys. **139**, 021102 (2013);

D. Kats, J. Chem. Phys. **141i**, 061101 (2014);

D. Kats, D. Kreplin, H.-J. Werner, F. R. Manby, J. Chem. Phys. **142**, 064111 (2015).

### Analytical energy gradients

Analytical gradients are now available for DCSD. Analytical gradients for CCSD(T), as well as for MP2-F12, CCSD(T)-F12, and DCSD-F12 are under development and will be made available free of charge at a later stage.

## **Orbital relaxed properties and analytical nuclear gradients for excited states**

Orbital relaxed properties, and analytical nuclear gradients for excited states are now available for local CC2 response and local ADC(2). This allows for geometry optimizations of excited states of large chromophores at these levels of theory. Furthermore, also local ADC(2) transition moments at the level of strict ADC(2) (which require second-order ground state singles and doubles) are available. For further reference see

K. Ledermüller, D.Kats and M. Schütz, *J. Chem. Phys.* **139**, 084111 (2013);  
 K. Ledermüller and M. Schütz, *J. Chem. Phys.* **140**, 164113 (2014);  
 M. Schütz, *J. Chem. Phys.* **142**, 214103 (2015).

## **PNO-LMP2 and PNO-LMP2-F12**

New parallel linear scaling PNO-LMP2 and PNO-LMP2-F12 programs as described in

H.-J. Werner, G. Knizia, C. Krause, and M. Schwilk, *J. Chem. Theory Comput.*, **11**, 484 (2015);  
 Q. Ma and H.-J. Werner, *J. Chem. Theory Comput.*, DOI: 10.1021/acs.jctc.5b00843 (2015);  
 C. Köppl and H.-J. Werner, *J. Chem. Phys.*, **142**, 164108 (2015).

are available in version 2015. PNO-LCCSD(T) is currently under development and will be made freely available to licensees of Molpro 2015 at a later stage.

## **Magnetizability and rotational g-tensor at DF-LMP2 level using GIAOs**

The program for NMR chemical shifts has been extended to include also magnetizability and rotational g-tensor. This is described in

S. Loibl and M. Schütz, *J. Chem. Phys.*, **141**, 024108 (2014).

## **Faster density fitting integral routines**

DFT and F12 methods with density fitting are significantly speeded up using improved integration routines written by G. Knizia.

## **Vibrational perturbation theory: VPT2**

A VPT2 program based on a semi-quartic force field (QFF) has been implemented, which allows for low-cost evaluations of anharmonic vibrational frequencies and associated vibrational constants. The determination of the QFF does not require analytical gradients (see the SURF program) and can thus be used in combination with any electronic structure method.

## **Vibrational multi-reference methods: VMSCF, VMRCI**

A suite of vibrational multi-reference methods is available now. Modals can be optimized at the VMSCF level [S. Heislbetz and G. Rauhut, *J. Chem. Phys.* **132**, 124102 (2012)] and correlation effects can be accounted for either variationally (VMRCI [F. Pfeiffer and G. Rauhut, *J. Chem. Phys.* **140**, 064110 (2014)]).

### **Anharmonic Franck-Condon factors: FCON**

A Franck-Condon program based on anharmonic vibrational wavefunctions has been implemented. Franck-Condon factors can either be computed by rotating the vibrational wavefunction or by transforming the potential energy surface in order to account for Duschinsky effects. This program, which allows for the accurate calculation of photoelectron spectra (absorption and fluorescence) relies on the newly developed transformation program SURFTRANS [P. Meier and G. Rauhut, *J. Chem. Phys.* (2015)].

### **Transformation of multi-dimensional potential energy surfaces: PESTRANS**

Multi-dimensional potential energy surfaces spanned in terms of normal coordinates - as computed with the SURF program - can now be rotated or transformed into an arbitrary set of normal coordinates. This allows for the efficient calculation of Franck-Condon factors or the calculation of vibrational spectra of isotopologues from just one potential energy surface [P. Meier, D. Oschetzki, R. Berger and G. Rauhut, *J. Chem. Phys.* **140**, 184111 (2014)].

### **Localized normal coordinates**

Within the SURF program, multi-dimensional potential energy surfaces can now alternatively be spanned in terms of localized normal coordinates. Three localization schemes are offered: (a) localization of the CH-stretching modes only and (b) localization of all normal coordinates to the subunits in molecular cluster calculations or (c) both. All localization schemes are symmetry sensitive.

### **Calculation of arbitrary vibrational states: VIBSTATE**

In the old Molpro release the calculation of vibrational states was limited to fundamentals, first vibrational overtones and simple combination bands. The new VIBSTATE program allows to specify arbitrary vibrational states, but the user must take care, that the parameters in the SURF program and the vibrational correlation programs are adjusted accordingly.

### **Raman scattering activities**

Raman scattering activities can now be computed within all vibrational SCF and vibration correlation programs. As polarizabilities can only be determined at the Hartree-Fock level, the accuracy is currently still limited.

### **Reaction databases**

A facility is provided to store and interrogate sets of molecules, together with information about how they are to be combined in balanced chemical equations. This database can be generated manually, or partially by running appropriate MOLPRO calculations. Analysis of the database can give a summary of the energy changes associated with each described reaction, and two or more similar databases can be compared reaction by reaction, to give a statistical analysis of the differences between them. Several common databases are included.

### 0.0.1 New density-fitting DFT-SAPT program

A new DFT-SAPT program has been implemented in Molpro which can be used in conjunction with monomer-centered (MCBS), monomer-centered plus (MC+BS) or dimer-centered (DCBS) basis sets. Even in DCBS mode fairly large complexes with about 800 electrons can be studied with this program, see A. Heßelmann and T. Korona. *J. Chem. Phys.* **141**, 094107 (2014).

### New features of MOLPRO2012.1

A summary of the features in Molpro can be found in a recent review: H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, and M. Schütz, *Molpro – a general purpose quantum chemistry program package*, *WIREs Comput. Mol. Sci.* **2**, 242 (2012), doi:10.1002/wcms.82.

The new features of MOLPRO version 2012.1 include the following.

#### Quasi-variational coupled-cluster theory

This modification of standard CCSD is capable of robustly describing chemical bond breaking with a single Hartree-Fock reference determinant (see J. B. Robinson and P. J. Knowles, *J. Chem. Phys.* **136**, 054114 (2012), doi:10.1063/1.3680560). It is implemented for closed-shell systems, with either the Brueckner condition or energy optimisation for the determination of orbitals. Triple excitations can be included perturbatively, BQVCCD (T) or OQVCCD (T) (J. B. Robinson and P. J. Knowles, *Phys. Chem. Chem. Phys.* **14**, 6729-6732 (2012), doi:10.1039/C2CP40698E; *J. Chem. Theor. Comput.* **8**, 2653-2660 (2012), doi:10.1021/ct300416b).

#### A new internally contracted MRCI code: MRCIC

A new internally contracted MRCI code [see K. R. Shamasundar, G. Knizia, and H.-J. Werner, *A new internally contracted multi-reference configuration interaction (MRCI) method*, *J. Chem. Phys.* **135**, 054101 (2011)] is now available. As compared to the old MRCI code it has the following advantages: (i) inactive orbitals (correlated in MRCI but closed-shell in the reference function) are treated explicitly, i.e., no density matrices and coupling coefficients need to be computed that involve these orbitals. Thus, in principle any number of inactive orbitals can be correlated, without the previously existing limitation to 32 correlated orbitals. Furthermore, additional configuration spaces are internally contracted (as in the RS2C code), resulting in a much improved efficiency, particularly for cases with many inactive orbitals. Currently, the method is implemented only for single-state calculations, but an extension to multi-state cases is under development and will be provided in the near future.

#### Explicitly correlated multireference theories: RS2-F12, MRCI-F12

Explicitly correlated multireference theories (CASPT2-F12, MRCI-F12) as described in T. Shiozaki and H.-J. Werner, *Communication: Second-order multireference perturbation theory with explicit correlation: CASPT2-F12*, *J. Chem. Phys.* **133**, 141103 (2010); T. Shiozaki, G. Knizia, and H.-J. Werner, *Explicitly correlated multireference configuration interaction: MRCI-F12*, *J. Chem. Phys.* **134**, 034113 (2011); T. Shiozaki and H.-J. Werner, *Explicitly correlated multireference configuration interaction with multiple reference functions: Avoided crossings and conical intersections*, *J. Chem. Phys.* **134**, 184104 (2011) lead to much improved convergence of the correlation energies with the basis set size. Explicitly correlated version of the RS2C and MRCIC codes are not yet available but will be made available as soon as possible.

A review of the explicitly correlated multireference methods can be found in T. Shiozaki and H.-J. Werner, *Mol. Phys.* **111**, 607 (2013).

### Extended multi-state CASPT2

Extended multistate CASPT2 (XMS-CASPT2) [see T. Shiozaki, W. Győrffy, P. Celani, and H.-J. Werner, *Communication: The extended multi-state CASPT2 method: Energy and nuclear gradients*, *J. Chem. Phys.* **135**, 081106 (2011)] provides a better description of near degenerate situations and avoided crossings. Currently this option is available only with the RS2 code, not for RS2C.

### Density fitted CASSCF and CASPT2

CASSCF and CASPT2 as well as the corresponding analytical gradient theories are now available with density fitting (DF-CASSCF, DF-RS2). See details in W. Győrffy, T. Shiozaki, G. Knizia, and H.-J. Werner, *Analytical energy gradients for second-order multireference perturbation theory using density fitting*, *J. Chem. Phys.* **138**, 104104 (2013).

### Extensions of explicitly correlated coupled-cluster methods

The (F12\*) approximation proposed by Hättig et al. [*J. Chem. Phys.* **132**, 231102 (2010)] has been implemented for closed-shell cases (in Molpro, this is denoted F12c). Other recent work (partly already included in Molpro2010.1) is described in H.-J. Werner, G. Knizia, and F. R. Manby, *Explicitly correlated coupled-cluster methods with pair-specific geminals*, *Mol. Phys.* **109**, 407 (2011); K. A. Peterson, C. Krause, H. Stoll, J. G. Hill, and H.-J. Werner, *Application of explicitly correlated coupled-cluster methods to molecules containing post-3d main group elements*, *Mol. Phys.* **109**, 2607 (2011) for alternative approximations.

Further basis sets of K. A. Peterson and J.G. Hill for explicitly correlated methods have been included. In particular these include the aug-cc-pVnZ-PP/OptRI and aug-cc-pwCVnZ-PP/OptRI sets for the group 11 and 12 transition metals. A full set of F12 basis sets for the *p*-block elements Ga-Rn will be added in the very near future. For recent work on molecules containing transition metals see D. H. Bross, J. G. Hill, H.-J. Werner, and Kirk A. Peterson, *Explicitly correlated composite thermochemistry of transition metal species*, *J. Chem. Phys.* **139**, 094302 (2013).

### Density fitted local coupled-cluster methods: DF-LCCSD(T), DF-LUCCSD(T), DF-LRPA

The local coupled cluster methods have been further improved. See H.-J. Werner and M. Schütz, *An efficient local coupled-cluster method for accurate thermochemistry of large systems*, *J. Chem. Phys.* **135**, 144116 (2011) for a description of the current implementation. An open-shell implementation [DF-LUCCSD(T)] is now also available (Y. Liu and H.-J. Werner, to be published.) Furthermore, the direct random phase approximation (RPA) has been implemented as a local method and using density fitting. Direct RPA can be considered as a CCD method reduced to only ring diagrams. In contrast to MP2 it also contains higher-order diagrams which e.g. cover Axilrod-Teller terms in intermolecular calculations. It is therefore especially attractive to replace in LCC calculations the LMP2 method for weak pairs by LRPA. This is now possible in our LCC code (O. Masur and M. Schütz, to be published.)

### Local coupled-cluster methods with orbital-specific virtual orbitals: OSV-LCCSD(T)

Local coupled cluster methods can optionally use orbital specific virtual orbitals (OSVs), see J. Yang, G. K. L. Chan, F. R. Manby, M. Schütz, and H.-J. Werner, *The orbital-specific virtual local coupled-cluster singles and doubles method: OSV-LCCSD*, J. Chem. Phys. **136**, 144105 (2012). The main advantage of this method is that the accuracy of the domain approximation can be controlled by a single parameter. Further developments that also use pair-natural orbitals (PNOs) as described in C. Krause and H.-J. Werner, *Perspective: Comparison of explicitly correlated local coupled-cluster methods with various choices of virtual orbitals*, Phys. Chem. Chem. Phys. **14**, 7591-7604 (2012) are in progress. A preliminary parallel PNO-LMP2-F12 method is already available.

### Explicitly correlated local MP2 and CC methods: DF-LMP2-F12, DF-LCCSD(T)-F12

The explicitly correlated coupled cluster methods as described in H.-J. Werner, *Eliminating the domain error in local explicitly correlated second-order Møller-Plesset perturbation theory*, J. Chem. Phys. **129**, 101103 (2008); T. B. Adler, F. R. Manby, and H.-J. Werner, *Local explicitly correlated second-order perturbation theory for the accurate treatment of large molecules*, J. Chem. Phys. **130**, 054106 (2009); T. B. Adler and H.-J. Werner, *Local explicitly correlated coupled-cluster methods: Efficient removal of the basis set incompleteness and domain errors*, J. Chem. Phys. **130**, 241101 (2009); T. B. Adler and H.-J. Werner, *An explicitly correlated local coupled-cluster method for calculations of large molecules close to the basis set limit*, J. Chem. Phys. **135**, 144117 (2011) are available for closed-shell cases (an open-shell implementation will follow soon). In these methods the errors of the local domain approximation are eliminated to a large extent, and the same accuracy as with the corresponding canonical methods can be achieved, even for molecules with 50-100 atoms.

### Improved DFT with density fitting

The efficiency of density functional theory has been much improved. In particular, the density fitting (DF-RKS, DF-UKS) codes for analytical energy gradients are now very much faster, due to a new integral code (adaptive integral core, AIC) written by G. Knizia. Some benchmarks can be found in H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, and M. Schütz, *Molpro – a general purpose quantum chemistry program package*, WIREs Comput. Mol. Sci. **2**, 242 (2012).

### Additional density functionals

A large number of additional density functionals has been added, including PBE0, PBEREV, M05, M05-2X, M06, M06-2X, M06-L, M06-HF, M08-HX, M08-SO, M11-L, SOGGA, SOGGA11, SOGGA11-X. (M11 is currently not available, but will likely be added in the near future).

### Additional gradient theories: CCSD, DF-MP2, DF-CASSCF, DF-RS2

New analytical gradient codes are now available for DF-MP2, DF-CASSCF, DF-RS2 (including MS and XMS options, also without density fitting), and for CCSD.

## Local methods for excited states

First-order properties of excited states via time-dependent Local CC2 linear response theory and ADC(2) are now also available for triplet states. This is described in K. Freundorfer, D. Kats, T. Korona, and M. Schütz, *Local CC2 response method for triplet states based on Laplace transform: Excitation energies and first-order properties*, J. Chem. Phys. **133**, 244110 (2010);

## NMR shielding tensors at DF-LMP2 level using GIAOs

An efficient method for calculating NMR shielding tensors at the local MP2 level has been implemented. Gauge including atomic orbitals (GIAOs) are used to eliminate the gauge origin dependence. Density fitting is employed to factorize the relevant electron repulsion integrals and their derivatives w.r. to the magnetic field. So far, the method has been already applied to systems with more than 2500 contracted basis functions and 300 correlated electrons. Relevant publications are S. Loibl, F. R. Manby, and M. Schütz, *Density fitted, local Hartree-Fock treatment of NMR chemical shifts using London atomic orbitals*, Mol. Phys., **108**, 477 (2010), and S. Loibl and M. Schütz, *NMR shielding tensors for density fitted local second-order Møller-Plesset perturbation theory using gauge including atomic orbitals*, J. Chem. Phys., **137**, 084107 (2012).

## SAPT(CCSD)

Symmetry-adapted perturbation theory of intermolecular interactions with monomers described in the CCSD level.

## Improved SCF algorithms for high-spin open-shell systems

For open-shell systems, RHF and RKS now use a two-step diagonalization process by default: Here the beta orbitals are found by a second diagonalization in the subspace of occupied alpha orbitals. This process usually leads to more stable convergence in difficult cases, compared to the standard diagonalization of a single open-shell Fock matrix (the latter behavior is recovered by {rhf,algo=0}). An additional section with suggestions for dealing with difficult cases has been added to be manual under “The SCF program”. Additionally, various limitations of the SCF program have been lifted. In particular, {rhf; maxit,1} now always works, and just calculates a Fock matrix and energy from the input orbitals, without updating said orbitals.

## FCIQMC: Stochastic Full CI

The FCIQMC program exists through an interface to the NECI codebase, which is actively developed in the group of A. Alavi, and has been integrated in to the MOLPRO code. The FCIQMC method is a recently introduced stochastic method which can calculate in principle FCI-quality energies for small to medium-sized molecules. See G. H. Booth, A. J. W. Thom, and A. Alavi, J. Chem. Phys. **131**, 054106 (2009); D. M. Cleland, G. H. Booth, and A. Alavi, J. Chem. Phys. **134**, 024112 (2011); G. H. Booth, D. M. Cleland, A. J. W. Thom, and A. Alavi, J. Chem. Phys. **135**, 084104 (2011).

## Ab Initio Multiple Spawning Dynamics

The AIMS module implements the Ab Initio Multiple Spawning method to perform dynamics calculations on multiple electronic states. It can also be used quite generally for first prin-



principles molecular dynamics on a single electronic surface, provided that nuclear gradients are available. Currently, non-adiabatic dynamics is limited to CASSCF wavefunctions; however, MS-CASPT2 non-adiabatic dynamics (with an implementation of analytical MS-CASPT2 non-adiabatic couplings) will be provided in the very near future. See M. Ben-Nun and T. J. Martinez, Chem. Phys. Lett. **298**, 57 (1998); B. G. Levine, J. D. Coe, A. M. Virshup and T. J. Martinez, Chem. Phys. **347**, 3 (2008); T. Mori, W. J. Glover, M. S. Schuurman and T. J. Martinez, J. Phys. Chem. A **116**, 2808 (2012).

### Updated def2 basis sets

The partially augmented Turbomole basis sets def2-SVPD, def2-TZVPD, and def2-QZVPPD (Rappoport, Furche: J. Chem. Phys. **133**, 134105 (2010)) have been added to the library. Additionally, the recently developed dhf- variants of the def2- basis sets have been included (dhf-SVP, dhf-TZVPP, ..., Weigend, Baldes: J. Chem. Phys. **133**, 174102 (2010)); these are reoptimized versions for the more modern MDF effective core potentials (most elements used MDF ECPs already in def2- and are unchanged). Short names like TZVPP (without prefix) now refer to dhf- basis sets.

### Parallel builds merged

The MPP and MPPX builds of Molpro have been merged and the decision to run in MPP or MPPX mode made a run-time option. To build parallel Molpro the `-mpp` flag to configure should be used; the `-mppx` flag is no longer required or valid. When running parallel Molpro, the `--mpp` option (default) can be used to specify MPP mode, and the `--mppx` option for MPPX mode.

### Auto-build options for parallel configuration

New options for configuring parallel Molpro to run on a single node or workstation have been implemented. These options (see manual) are prefixed with `-auto`, and in conjunction with `-mpp` configure will download, build and install a variety of different prerequisites for parallel Molpro.

### New features of MOLPRO2010.1

The functionality is essentially the same as in 2009.1, but many bug fixes and small improvements have been added. Please note the following major changes, in particular of the default RI basis sets in explicitly correlated methods as described below.

### AIC density fitting integral program

A faster integral program for density fitting, written by Gerald Knizia, has been added. In particular this speeds up the integral evaluation in F12 calculations by up to a factor of about 10 (depending on the basis set). This program is now used by default, but can be disabled by setting

```
dfit,aic=0
```

in the beginning of the input.

## Pair specific geminal exponents in explicitly correlated methods

Different exponents for the Slater-type geminals can be used for valence-valence, core-valence, and core-core pairs. See manual for details.

## Change of defaults in explicitly correlated methods

For explicitly correlated F12 calculations that use the VnZ-F12 orbital basis sets (OBS), it is now the default to use the corresponding VnZ-F12/OPTRI basis sets to construct the complementary auxiliary orbital basis (CABS). In case that CABS is not used (e.g., in LMP2-F12), the OBS and OPTRI sets are merged automatically. This yields exactly the same results as would be obtained with the CABS approach. In order to use the default RI sets of 2009.1, please specify option `RI_BASIS=JKFIT` on the command line, or

```
explicit, ri_basis=jkfit
```

For compatibility reasons, it is still the default to use the JKFIT sets as RI basis for the AVnZ orbital basis sets. In order to use the corresponding OPTRI sets (where available) please specify option `RI_BASIS=OPTRI`.

## New basis sets in the Molpro library

A number of new basis sets have been added to the Molpro library since version 2009.1. The references for these sets can be found in the headers of the respective libmol files.

Li, Be, Na, Mg:

a) New official versions of the correlation consistent basis sets for these elements have been added, both non-relativistic and those contracted for Douglas-Kroll relativistic calculations. Specifically these are:

`cc-pVnZ (n=D-5)` `cc-pwCVnZ (n=D-5)` `aug-cc-pVnZ (n=D-5)` `aug-cc-pwCVnZ (n=D-5)`

and the above with a -DK extension. The older `cc-pVnZ` basis sets for these elements can still be accessed via the keywords `vdz-old`, etc.

b) New basis sets, including RI and MP2 auxiliary sets, have been added for F12 explicit correlation calculations:

`cc-pVnZ-F12 (n=D-Q)` `cc-pCVnZ-F12 (n=D-Q)`

The optimized CABS auxiliary sets have the same name but with a /OptRI context

For MP2 and CCSD auxiliary sets, the `cc-pVnZ/MP2FIT` sets of Hättig can be used, but a new `cc-pV5Z/MP2FIT` set has been added that is optimal for the new `cc-pV5Z` basis set; new `aug-cc-pVnZ/MP2FIT (n=D-5)` sets have been added as well. The original `cc-pV5Z/MP2FIT` sets of Hättig have been renamed `v5z-old/mp2fit`.

Cu-Zn, Y-Cd, Hf-Hg:

a) While the `aug-cc-pVnZ-PP (n=D-5)` and `cc-pwCVnZ-PP (n=D-5)` sets were already available, the combination `aug-cc-pwCVnZ-PP` was not yet defined. These have now been added for these elements.

b) Triple-zeta DK sets have been included now for all of these elements. Unless otherwise noted, these were optimized for 2nd-order

DKH. In the cases of Hf-Hg, sets contracted for 3rd-order DKH are also now included:

cc-pVTZ-DK cc-pwCVTZ-DK aug-cc-pVTZ-DK aug-cc-pwCVTZ-DK

and the above with -DK replaced by -DK3 for DKH3 calculations in the case of Hf-Hg.

H-He, B-Ne, Al-Ar, Ga-Kr: a) A variety of DK contracted basis sets have been added for these elements:

aug-cc-pVnZ-DK (n=D-5) cc-pCVnZ-DK (n=D-5) cc-pwCVnZ-DK (n=D-5) aug-cc-pCVnZ-DK (n=D-5) aug-cc-pwCVnZ-DK (n=D-5)

b) Official cc-pCV6Z and aug-cc-pCV6Z are now also available for Al-Ar

c) For explicitly correlated calculations, the core-valence sets have been added:

cc-pCVnZ-F12 (n=D-Q) for B-Ne, Al-Ar cc-pCVnZ-F12/OptRI (n=D-Q) for B-Ne, Al-Ar

d) cc-pVnZ-F12/OptRI (n=D-Q) as also been added for He

Turbomole def2 basis sets: The complete Turbomole def2 basis set family has been added to the Molpro basis library (for all elements H to Rn, except Lanthanides). The def2-orbital basis sets can now be accessed as SV(P), SVP, TZVP, TZVPP, QZVP and QZVPP. In this nomenclature SVP, TZVPP, and QZVPP correspond to valence double-zeta (VDZ), valence triple-zeta (VTZ) and valence quadruple-zeta (VQZ) basis sets, respectively.

Auxiliary density fitting basis sets for all elements are available as well (e.g., TZVPP/JFIT, TZVPP/JKFIT, TZVPP/MP2FIT) and are chosen automatically in density-fitted calculations. Supposedly, the JKFIT sets are universal and also applicable in combination with the AVnZ basis sets. Initial results indicate that they also work well with the cc-pVnZ-PP and aug-cc-pVnZ-PP series of basis sets.

The orbital basis sets can also be accessed in singly and doubly augmented versions (carrying A or DA prefixes, respectively, e.g., ASVP, DASVP), and the auxiliary fitting sets in singly augmented versions (e.g., ATZVPP/MP2FIT).

The old Turbomole basis sets have been renamed; if required, they can be accessed with a def1-prefix (e.g., def1-SVP, def1-TZVPP, etc.).

### **Improved support for MPI implementation of parallelism**

The *ppidd* harness that manages interprocess communication has been improved. The performance of the implementation based on pure MPI, as an alternative to use of the Global Arrays toolkit, is considerably improved, through the use of dedicated helper processes that service one-sided remote memory accesses.

### **Change of the order of states and the defaults for computing the Davidson correction in multi-state MRCI**

The previous way to compute the Davidson correction in multi-state MRCI could lead to non-continuous cluster corrected energies. This is now avoided by ordering the MRCI eigenstates

according to increasing energy (previously they were ordered according to maximum overlap with the reference wavefunctions). Furthermore, additional options for computing the Davidson correction in multi-state calculations are added (for details see manual). The old behavior can be recovered using options SWAP,ROTREF=-1.

### **IPEA shift for CASPT2**

A variant of the IPEA shift of G. Ghigo, B. O. Roos, and P.A. Malmqvist, Chem. Phys. Lett. **396**, 142 (2004) has been added. The implementation is not exactly identical to the one in MOLCAS, since in our program the singly external configurations are not (RS2) or only partially (RS2C) contracted. The shift is invoked by giving option IPEA=*shift* on the RS2 or RS2C commands; the recommended value for *shift* is 0.25. For details of the implementation see manual.

### **Karton-Martin extrapolation of HF energies**

The two-point formula for extrapolating the HF reference energy, as proposed by A. Karton and J. M. L. Martin, Theor. Chem. Acc. **115**, 330 (2006) has been added:  $E_{\text{HF},n} = E_{\text{HF,CBS}} + A(n+1) \cdot \exp(-9\sqrt{n})$ . Use METHOD\_R=KM for this.

## **New features of MOLPRO2009.1**

### **Basis set updates**

Correlation consistent basis sets for Li, Be, Na, and Mg have been updated to their official versions as reported in Prascher et al., Theor. Chem. Acc. (2010). These now also include core-valence, diffuse augmented, and Douglas-Kroll relativistically contracted versions. The previous sets are still available but have been renamed vdz-old, vtz-old, etc.

### **Explicitly correlated calculations**

Due to new findings, the default behavior of the F12 programs was changed in the following points:

1. For open-shell systems the default wave function ansatz for was modified. This affects RMP2-F12 and open-shell CCSD-F12 calculations. The new default generally improves open-shell treatments and leads to more consistent behavior. The previous behavior can be restored by

```
explicit,extgen=0
```

(for more details see manual).

2. The procedure for the construction of complementary auxiliary basis sets (CABS) and the thresholds were changed. This affects all non-local F12 calculations. The previous behavior can be restored by

```
explicit,ortho_cabs=0,thrcabs=1-7,thrcabs_rel=1e-8
```

3. In numeric frequency calculations, the freezing of auxiliary basis sets was improved. This can affect calculations where many redundant functions are deleted.

4. Pair energies for the explicitly correlated methods can be printed using

```
print,pairs
```

If inner-shell orbitals are correlated, the cc, cv, and vv contributions to the correlation energies are also printed.

### Improvements to the Hartree-Fock program

The atomic density guess in Hartree-Fock has been improved and extended. Guess basis sets are now available for most atoms and for all pseudopotentials. Most pseudopotentials have been linked to the appropriate basis sets, so that it is sufficient to specify, e.g.

```
basis=vtz-pp
```

which will select the correlation consistent triple zeta basis sets and the associated (small core) pseudopotential. Similarly, it is mostly sufficient to specify the basis set for other pseudopotential/basis set combinations.

If the wavefunction symmetry is not given in the Hartree-Fock input and not known from a previous calculation, the HF program attempts to determine it automatically from the aufbau principle (previously, symmetry 1 was assumed in all cases). For example,

```
geometry={n};
{hf;wf,spin=3}
```

automatically finds that the wavefunction symmetry is 8.

### Changes to geometry input

1. Rationalisation of options for molecular geometry. It is now illegal to specify symmetry and orientation options (eg x;noorient;angstrom) inside a geometry block, which now contains just the geometry specification (Z-matrix or XYZ). Options have to be specified using the new ORIENT and SYMMETRY commands, and/or existing commands such as ANGSTROM. This change will, unfortunately, render many inputs incompatible with 2008.1 and earlier versions of Molpro, but has been introduced to allow correct and clean parsing of geometries containing, for example, yttrium atoms, which previously conflicted with the Y symmetry option.
2. Simplification of geometry input. The program now detects automatically whether the geometry is specified as a Z-matrix, or using cartesian coordinates, and so there is no need any more to set the geomtyp variable. The standard XYZ format is still accepted for cartesian coordinates, but the first two lines (number of atoms, and a comment) can be omitted if desired.

### MPI-2 parallel implementation

The program now can be built from the source files with the Global Arrays toolkit or the MPI-2 library for parallel execution.

## **New features of MOLPRO2008.1**

The new features of MOLPRO version 2008.1 include the following.

1. Efficient closed-shell and open-shell MP2-F12 and CCSD(T)-F12 methods which dramatically improve the basis set convergence, as described in *J. Chem. Phys.* 126, 164102 (2007); *ibid.* 127, 221106 (2007); *ibid.* 128, 154103 (2008).
2. Natural bond order (NBO) and natural population analysis (NPA) as described in *Mol. Phys.* 105, 2753 (2007) and references therein.
3. Correlation regions within a localized molecular orbital approach as described in *J. Chem. Phys.* 128, 144106 (2008).
4. Automated calculation of anharmonic vibrational frequencies and zero-point energies using VCI methods as described in *J. Chem. Phys.* 126, 134108 (2007) and references therein.
5. Coupling of DFT and coupled cluster methods as described in *Phys. Chem. Chem. Phys.* 10, 3353 (2008) and references therein.
6. Enhanced connections to other programs, including graphical display of output and 3-dimensional structures.
7. Support for latest operating systems and compilers, including Mac OS X.

## **New features of MOLPRO2006.1**

Features and enhancements in MOLPRO version 2006.1 most notably included efficient density fitting methods, explicitly correlated methods, local coupled cluster methods, and several new gradient programs: following:

1. More consistent input language and input pre-checking.
2. More flexible basis input, allowing to handle multiple basis sets
3. New more efficient density functional implementation, additional density functionals.
4. Low-order scaling local coupled cluster methods with perturbative treatment of triples excitations (LCCSD(T) and variants like LQCISD(T))
5. Efficient density fitting (DF) programs for Hartree-Fock (DF-HF), Density functional Kohn-Sham theory (DF-KS), Second-order Møller-Plesset perturbation theory (DF-MP2), as well as for all local methods (DF-LMP2, DF-LMP4, DF-LQCISD(T), DF-LCCSD(T))
6. Analytical QCISD(T) gradients
7. Analytical MRPT2 (CASPT2) and MS-CASPT2 gradients, using state averaged MCSCF reference functions
8. Analytical DF-HF, DF-KS, DF-LMP2, and DF-SCS-LMP2 gradients
9. Explicitly correlated methods with density fitting: DF-MP2-R12/2A', DF-MP2-F12/2A' as well as the local variants DF-LMP2-R12/2\*A(loc) and DF-LMP2-F12/2\*A(loc).
10. Coupling of multi-reference perturbation theory and configuration interaction (CIPT2)

11. DFT-SAPT
12. Transition moments and transition Hamiltonian between CASSCF and MRCI wavefunctions with different orbitals.
13. A new spin-orbit integral program for generally contracted basis sets.
14. Douglas-Kroll-Hess Hamiltonian up to arbitrary order.
15. Improved procedures for geometry optimization and numerical Hessian calculations, including constrained optimization.
16. Improved facilities to treat large lattices of point charges for QM/MM calculations, including lattice gradients .
17. An interface to the MRCC program of M. Kallay, allowing coupled-cluster calculations with arbitrary excitation level.
18. Automatic *embarrassingly parallel* computation of numerical gradients and Hessians (m<sub>ppx</sub> Version).
19. Additional parallel codes, e.g. DF-HF, DF-KS, DF-LCCSD(T) (partly, including triples).
20. Additional output formats for tables (XHTML, L<sup>A</sup>T<sub>E</sub>X, Maple, Mathematica, Matlab and comma-separated variables), orbitals and basis sets (XML), and an optional well-formed XML output stream with important results marked up.

### **New features of MOLPRO2002.6**

Relative to version 2002.1, there are the following changes and additions:

1. Support for IA-64 Linux systems (HP and NEC) and HP-UX 11.22 for IA-64 (Itanium2).
2. Support for NEC-SX systems.
3. Support for IBM-power4 systems.
4. Modified handling of Molpro system variables. The SET command has changed .
5. The total charge of the molecule can be specified in a variable CHARGE or on the WF card .
6. Improved numerical geometry optimization using symmetrical displacement coordinates .
7. Improved numerical frequency calculations using the symmetry (AUTO option .

### **New features of MOLPRO2002**

Relative to version 2000.1, there are the following principal changes and additions:

1. Modules direct and local are now included in the base version. This means that integral-direct procedures as described in  
M. Schütz, R. Lindh, and H.-J. Werner, Mol. Phys. 96, 719 (1999),  
linear-scaling local MP2, as described in

G. Hetzer, P. Pulay, and H.-J. Werner, Chem. Phys. Lett. 290, 143 (1998),  
 M. Schütz, G. Hetzer, and H.-J. Werner, J. Chem. Phys. **111**, 5691 (1999),  
 G. Hetzer, M. Schütz, H. Stoll, and H.-J. Werner, J. Chem. Phys. **113**, 9443 (2000),

as well as LMP2 gradients as described in

A. El Azhary, G. Rauhut, P. Pulay, and H.-J. Werner, J. Chem. Phys. **108**, 5185 (1998)

are now available without special license. The linear scaling LCCSD(T) methods as described in

M. Schütz and H.-J. Werner, J. Chem. Phys. **114**, 661 (2001),

M. Schütz and H.-J. Werner, Chem. Phys. Lett. **318**, 370 (2000),

M. Schütz, J. Chem. Phys. **113**, 9986 (2000)

will be made available at a later stage.

2. QCISD gradients as described in Phys. Chem. Chem. Phys. **3**, 4853 (2001) are now available.
3. Additional and more flexible options for computing numerical gradients and performing geometry optimizations.
4. A large number of additional density functionals have been added, together with support for the automated functional implementer described in Comp. Phys. Commun. **136** 310–318 (2001).
5. Multipole moments of arbitrary order can be computed.
6. Further modules have been parallelized, in particular the CCSD(T) and direct LMP2 codes. The parallel running procedures have been improved. The parallel version is available as an optional module.
7. The basis set library has been extended.
8. Some subtle changes in the basis set input: it is not possible any more that several one-line basis input cards with definitions for individual atoms follow each other. Each new basis card supercedes previous ones. Either all specifications must be given on *one* BASIS card, or a basis input block must be used. BASIS, NAME is now entirely equivalent to BASIS=NAME, i.e. a global default basis set is defined and the variable BASIS is set in both cases.
9. Pseudopotential energy calculations can now be performed with up to *i*-functions, gradients with up to *h*-functions.
10. Many internal changes have been made to make MOLPRO more modular and stable. Support has been added for recent operating systems on Compaq, HP, SGI, SUN, and Linux. The patching system has been improved.

## Features that were new in MOLPRO2000

Relative to version 98.1, there are the following principal changes and additions:

1. There was a fundamental error in the derivation of the spin-restricted open-shell coupled-cluster equations in J. Chem. Phys. 99, 5129 (1993) that is also reflected in the RCCSD code in MOLPRO version 98.1 and earlier. This error has now been corrected, and an erratum has been published in J. Chem. Phys. **112**, 3106 (2000). Fortunately, the numerical



implications of the error were small, and it is not anticipated that any computed properties will have been significantly in error.

2. There was a programming error in the transformation of gradients from Cartesian to internal coordinates, which in some cases resulted in slow convergence of geometry optimizations. The error is now fixed.
3. Vibrational frequencies formerly by default used average atomic masses, rather than those of the most common isotopes, which is now the default behaviour.
4. MCSCF second derivatives (author Riccardo Tarroni) added (preliminary version, only without symmetry). Frequency and geometry optimization programs are modified so that they can use the analytic Hessian.
5. New internally contracted multi-reference second-order perturbation theory code (author Paolo Celani) through command `RS2C`, as described in P. Celani and H.-J. Werner, *J. Chem. Phys.* **112**, 5546 (2000).
6. EOM-CCSD for excited states (author Tatiana Korona).
7. QCISD dipole moments as true analytical energy derivatives (author Guntram Rauhut).
8. Linear scaling (CPU and memory) LMP2 as described by G. Hetzer, P. Pulay, and H.-J. Werner, *Chem. Phys. Lett.* **290**, 143 (1998).  
M. Schütz, G. Hetzer, and H.-J. Werner, *J. Chem. Phys.* **111**, 5691 (1999).
9. Improved handling of basis and geometry records. 98.1 and 99.1 dump files can be restarted, but in case of problems with restarting old files, add `RESTART, NOGEOM` immediately after the `file` card. Also, if there are unjustified messages coming up in very large cases about "ORBITALS CORRESPOND TO DIFFERENT GEOMETRY" try `ORBITAL,record,NOCHECK`. (This can happen for cases with more than 100 atoms, since the old version was limited to 100).
10. Reorganization and generalization of basis input. Increased basis library.
11. Counterpoise geometry optimizations.
12. Improved running procedures for MPP machines. Parallel direct scf and scf gradients are working. These features are only available with the MPP module, which is not yet being distributed.
13. Important bugfixes for DFT grids, CCSD with paging, finite field calculations without core orbitals, spin-orbit coupling.
14. Many other internal changes.

As an additional service to the MOLPRO community, an electronic mailing list has been set up to provide a forum for open discussion on all aspects of installing and using MOLPRO. The mailing list is intended as the primary means of disseminating hints and tips on how to use Molpro effectively. It is not a means of raising queries directly with the authors of the program. For clearly demonstrable program errors, reports should continue to be sent to `molpro@molpro.net`; however, 'how-to' questions sent there will merely be redirected to this mailing list.

In order to subscribe to the list, send mail to `molpro-user-request@molpro.net` containing the text `subscribe`; for help, send mail containing the text `help`.

Messages can be sent to the list (molpro-user@molpro.net), but this can be done only by subscribers. Previous postings can be viewed in the archive at <http://www.molpro.net/molpro-user/archive> irrespective of whether or not you subscribe to the list. Experienced Molpro users are encouraged to post responses to queries raised. Please do contribute to make this resource mutually useful.

## Facilities that were new in MOLPRO98

MOLPRO98 has the full functionality of MOLPRO96, but in order to make the code more modular and easier to use and maintain, a number of structural changes have been made. In particular, the number of different records has been significantly reduced. The information for a given wavefunction type, like orbitals, density matrices, fock matrices, occupation numbers and other information, is now stored in a single dump record. Even different orbital types, e.g., canonical, natural, or localized orbitals, are stored in the same record, and the user can subsequently access individual sets by keywords on the `ORBITAL` directive. New facilities allow the use of starting orbitals computed with different basis sets and/or different symmetries for SCF or MCSCF calculations. The default starting guess for SCF calculations has been much improved, which is most useful in calculations for large molecules. The use of special procedures for computing non-adiabatic couplings or diabaticization of orbitals has been significantly simplified. We hope that these changes make the program easier to use and reduce the probability of input errors. However, in order to use the new facilities efficiently, even experienced MOLPRO users should read the sections *RECORDS* and *SELECTING ORBITALS AND DENSITY MATRICES* in the manual. It is likely that standard MOLPRO96 inputs still work, but changes may be required in more special cases involving particular records for orbitals, density matrices, or operators.

All one-electron operators needed to compute expectation values and transition quantities are now stored in a single record. Operators for which expectation values are requested can be selected globally for all programs of a given run using the global `GEXPEC` directive, or for a specific program using the `EXPEC` directive. All operators are computed automatically when needed, and the user does not have to give input for this any more. See section *ONE-ELECTRON OPERATORS AND EXPECTATION VALUES* of the manual for details.

Due to the changed structure of dump and operator records, the utility program `MATROP` has a new input syntax. MOLPRO96 inputs for `MATROP` do not work any more.

In addition to these organizational changes, a number of new programs have been added. Analytic energy gradients can now be evaluated for MP2 and DFT wavefunctions, and harmonic vibrational frequencies, intensities, and thermodynamic quantities can be computed automatically using finite differences of analytical gradients. Geometry optimization has been further improved, and new facilities for reaction path following have been added.

An interface to the graphics program `MOLDEN` has been added, which allows to visualize molecular structures, orbitals, electron densities, or vibrations.

Integral-direct calculations, in which the two-electron integrals in the AO basis are never stored on disk but always recomputed when needed, are now available for all kinds of wavefunctions, with the exception of perturbative triple excitations in MP4 and CCSD(T) calculations. This allows the use of significantly larger basis sets than was possible before. The direct option can be selected globally using the `GDIRECT` command, or for a specific program using the `DIRECT` directive. See section *INTEGRAL DIRECT METHODS* in the manual for details. Note that the `DIRECT` module is optional and not part of the basic MOLPRO distribution.

*Local* electron correlation methods have been further improved. In combination with the integral-direct modules, which implement efficient prescreening techniques, the scaling of the computational cost with molecular size is dramatically reduced, approaching now quadratic or even

linear scaling for MP2 and higher correlation methods. This makes possible to perform correlated calculations for much larger molecules than were previously feasible. However, since these methods are subject of active current research and still under intense development, we decided not to include them in the current MOLPRO release. They will be optionally available in one of the next releases.